New Aspects of Fluid Criticality:
The Yang-Yang Anomaly and Scaling with Pressure Mixing (Invited)

Michael E. Fisher
Institute for Physical Science and Technology
University of Maryland
College Park, MD 20742 U.S.A.

The standard thermodynamic description of a pure fluid near criticality invokes two "scaling fields," say , $\tilde{t}$ and $\tilde{\mu}$, which mix temperature, T and chemical potential, μ. But is that adequate? Recent work* answers "No!" Specifically, (i) a careful analysis of the two-phase isochoric heat capacity of propane, (ii) a detailed grand canonical Monte Carlo study of a hard-core-square-well model, and (iii) an exact analysis of a novel *compressible cell gas* (extending the usual rigid lattice gas), demonstrate that the pressure, p, can *also* mix into $\tilde{t}$ and $\tilde{\mu}$.

A direct consequence, answering a question of Yang and Yang (1964), is that the chemical potential at coexistence, $\mu_\sigma(T)$, becomes singular when $t \propto (T - T_c) \to 0-$ with $d^2\mu_\sigma/dT^2$ diverging, in general, like $C_V \sim |t|^{-\alpha}$ with $\alpha \simeq 0.11$. Likewise, the coexistence-curve diameter, $\bar{\rho}(T) = ½\,(\rho_{\text{liq}} + \rho_{\text{gas}})$, has, in general, a singularity proportional to $(\rho_{\text{liq}} - \rho_{\text{gas}})^2 \sim |t|^{2\beta}$, with $\beta \simeq 0.326$; this *dominates* the previously accepted singularity $\sim |t|^{1-\alpha}$. In addition, current finite-size scaling techniques for analyzing simulations of near-critical fluids require modification.

*****With coworkers G. Orkoulas, A.Z. Panagiotopoulos, Y.-C. Kim, and C. Üstün.